



CH-110 Advanced General Chemistry I

Prof. A. Steinauer
angela.steinauer@epfl.ch

Indicative feedback

Feedback	Implementation
The course is too fast and too dense.	Study guide, summaries at the end of chapters.
Some concepts are not explained in much depth, and it is not clear which concepts are important.	Study guide, will upload formula sheet by end of November, exercises.
Provide slides before class.	
Provide summaries and highlight key points.	Study guide, summaries at the end of chapters.
Teaching style: blackboard is preferred over slides. More practical examples during class.	Will try to do more on blackboard/iPad.
English comprehension issues.	Subtitles, slides, TAs speak French.
Reduce noise level in lecture hall.	Will remind you more often.
Provide more mathematical explanations.	
Commitment and passion is appreciated.	Thank you!
Clarity of slides is appreciated.	Thank you!
Sexist answers during polls.	

Housekeeping notes

- The **electronegativities** of N and Cl are very similar. Which one is higher or lower depends on the periodic table you use, for example, for the one in the book, the electronegativity of $\text{Cl} > \text{N}$, but for the one in the classroom, $\text{N} > \text{Cl}$.

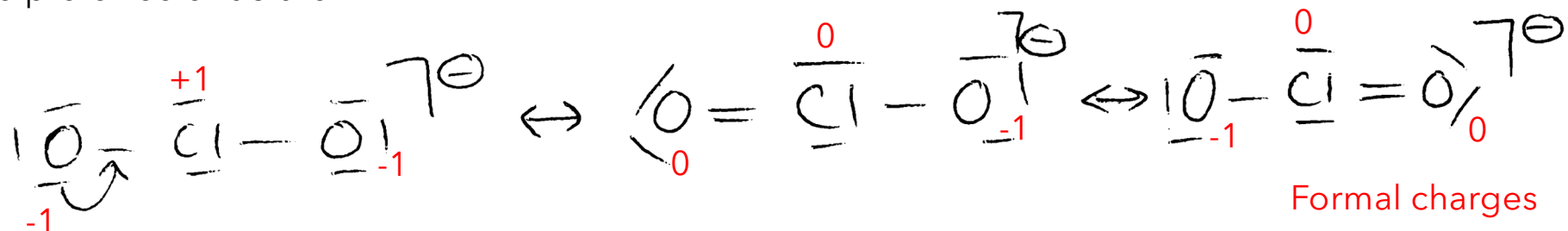
Electronegativity TREND: $\text{F} > \text{O} > \text{N/Cl} > \text{Br} > \text{I} > \text{S} > \text{C/Se} > \text{H} > \dots$

- **Exercise today:** 5.8 and 5.9 plus série 6
- **Exercise 3:** we had another look at exercise 3.4, it doesn't make sense. If you want to practice this chapter, I recommend focusing on exercises 1D.3, 1.9, 1.33 from the book.
- Annotated study guide for chapter 1 is uploaded on Moodle.
- **No office hours today.** Please email me if you have questions that the TAs cannot answer.

2B.1: Lewis structures

Student question

The Lewis structure of chlorite ion could also have a double bond, why is the structure shown in class the preferred structure?



The first satisfies the octet rule. The 2nd and 3rd structure contain hypervalent chlorine. Which one is closest to the truth? Analysis of formal charges suggests 2nd and 3rd. Additionally, look at bond lengths:

Cl–O (single bond): 172 pm

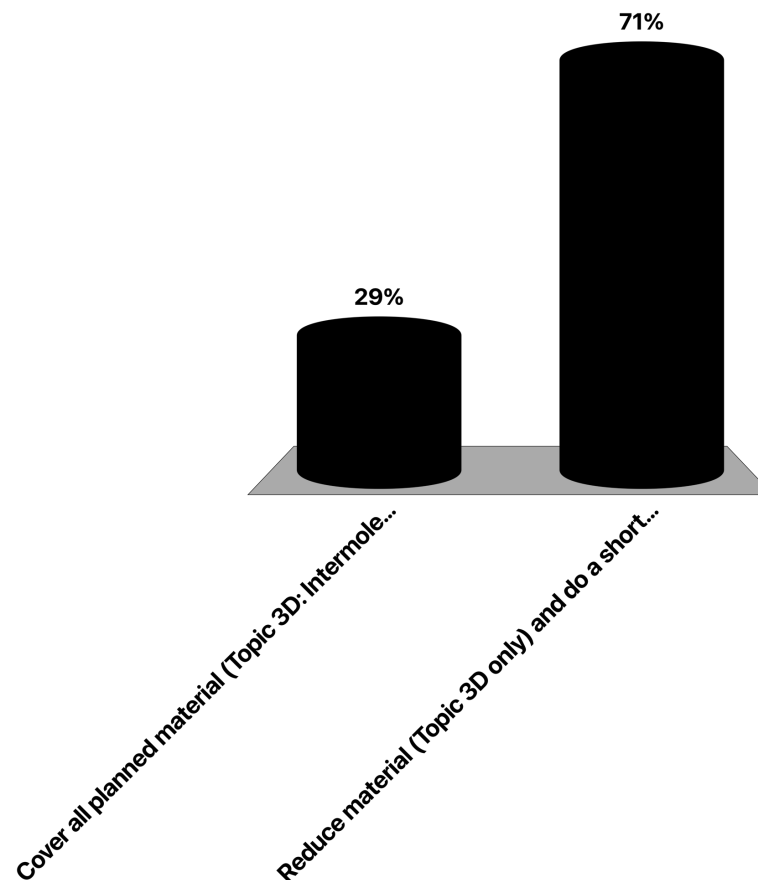
Cl=O (double bond): 140 pm

Cl–O in ClO_2^- : 156 pm $\rightarrow$ Chlorite has a bond order between 1 and 2.

What do you prefer?

A. Cover all planned material (Topic 3D: Intermolecular Forces, 3F: Liquids, 3G: Solids)

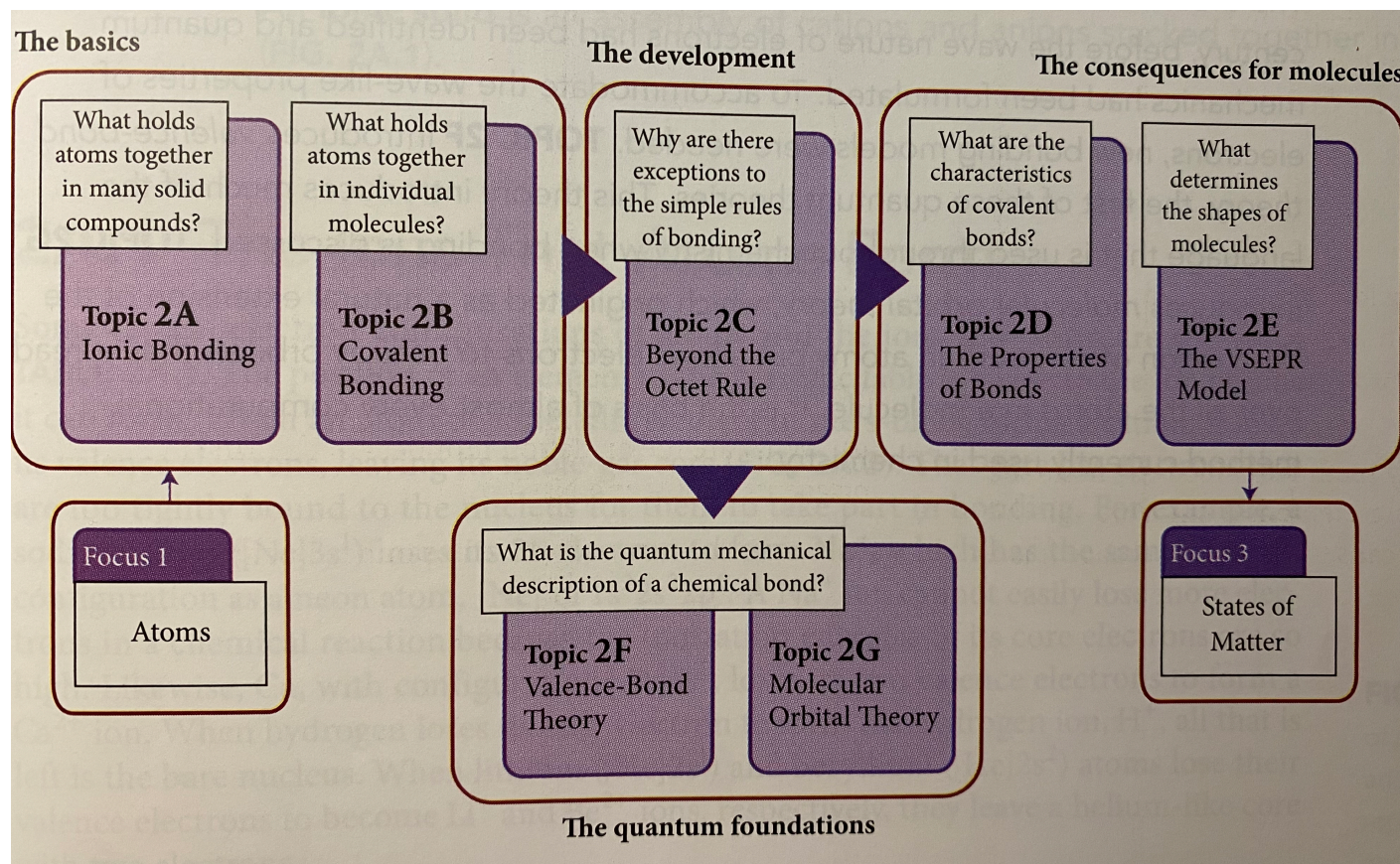
B. Reduce material (Topic 3D only) and do a **short practice exam** in class (not graded)



Link: www.responseware.eu

Session ID: 124362

Overview Chapter 2 (Focus 2: Bonds Between Atoms)



The Properties of Bonds

Topic 2D

Topic 2D.1 Correcting the covalent model: electronegativity

Topic 2D.2 Correcting the ionic model: polarizability

Topic 2D.3 Bond strengths

Topic 2D.4 Bond lengths

WHY DO YOU NEED TO KNOW THIS MATERIAL?

- Properties of bonds vary widely. Variations in bond strength, bond length, and the distribution of electrons in a bond, are used to explain the physical and chemical properties of molecules.

WHAT DO YOU NEED TO KNOW ALREADY?

- Periodic trends (Topic 1F)
- Concept of resonance (Topic 2B)
- Role of electron-pair sharing in covalent bonding (Topic 2B)

Correcting the Covalent Model: Electronegativity

Topic 2D.1

2D.1 Correcting the covalent model: electronegativity

Two extremes

Covalent bonding ←————→ Ionic bonding

Many compounds exist
somewhere in the middle

2D.1 Correcting the covalent model: electronegativity

Two extremes



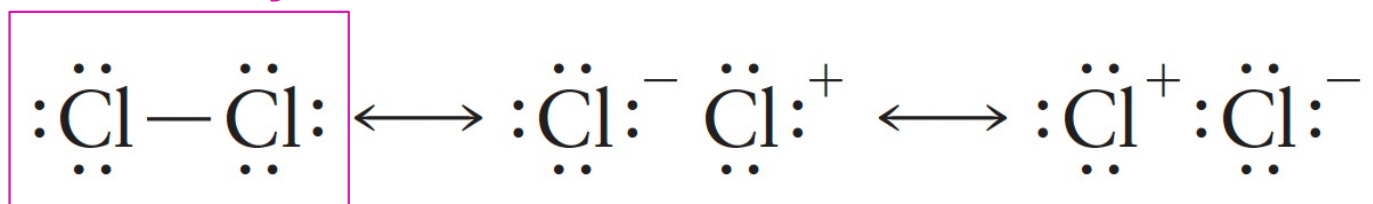
Covalent bonding $\longleftrightarrow$ Ionic bonding

All molecules should be
viewed as **resonance**
hybrids of purely covalent
and purely ionic structures

2D.1 Correcting the covalent model: electronegativity

Two extremes

More likely

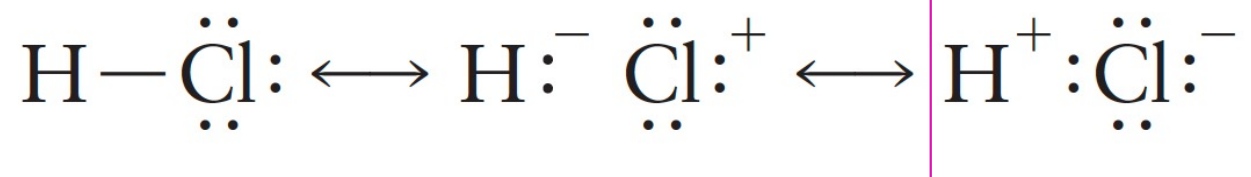


Covalent bonding



Ionic bonding

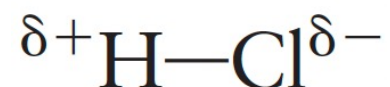
More likely



2D.1 Correcting the covalent model: electronegativity

Partial charges

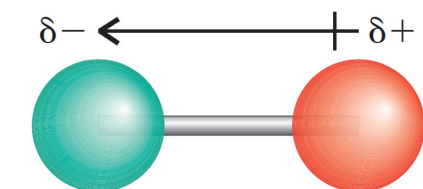
- Outcome of resonance favoring in H–Cl: small negative charge on Cl, small positive charge on H (**partial charges**)



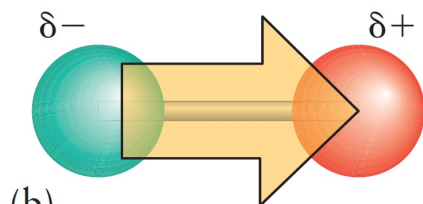
- A bond with nonzero partial charge: **polar covalent bond**
- A bond with zero partial charge: **nonpolar bond**

2D.1 Correcting the covalent model: electronegativity

Electric dipole



(a)



(b)

- **Partial charges** on the two atoms in polar covalent bond form **an electric dipole**.
- (a) Dipole represented by arrow that points to negative partial charge
- (b) Modern convention (used here): arrows point to positive partial charge
- **The electric dipole moment** (μ) describes the magnitude of an electric dipole, units: debye (D)

2D.1 Correcting the covalent model: electronegativity

Electronegativity (χ): Pauling vs. Mullikan

Electronegativity (χ) : **the electron-pulling power of an atom in a molecule**

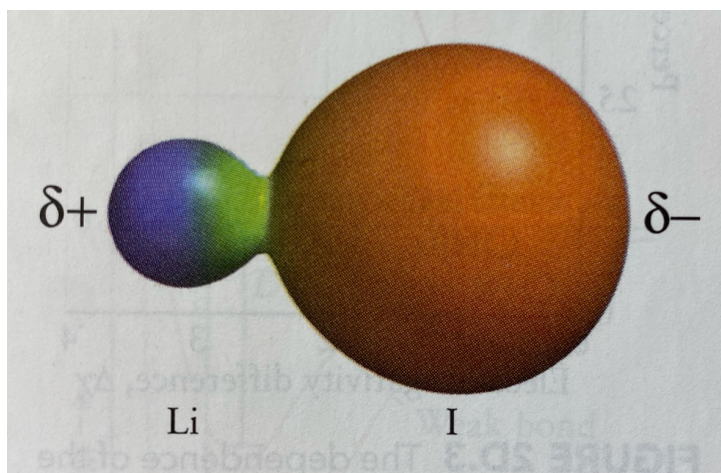


Figure 2D.1

2D.1 Correcting the covalent model: electronegativity

Electronegativity (χ): Pauling vs. Mullikan

- Pauling's electronegativities were based on dissociation energies between bonds.
- For two elements, A and B, what are the energies needed to break bonds A–A, B–B, and A–B.
- **Pauling** defined the difference in electronegativity of the two elements A and B as:

$$|\chi_A - \chi_B| = \left\{ D(A - B) - \frac{1}{2} [D(A - A) + D(B - B)] \right\} \text{ (no need to know by heart)}$$

- **Mullikan** (see Topic 1F.5) used a different strategy:

$$\chi = \frac{1}{2} (I_I + E_{ea})$$

Pauling and Mullikan's electronegativities are **qualitatively similar**.

2D.1 Correcting the covalent model: electronegativity

Electronegativity (χ): Pauling values

				H 2.20				18 He
	1	2	13	14	15	16	17	
2	Li 0.98	Be 1.57	B 2.04	C 2.55	N 3.04	O 3.44	F 3.98	Ne
3	Na 0.93	Mg 1.31	Al 1.61	Si 1.90	P 2.19	S 2.58	Cl 3.16	Ar
4	K 0.82	Ca 1.00	Ga 1.81	Ge 2.01	As 2.18	Se 2.55	Br 2.96	Kr
5	Rb 0.82	Sr 0.95	In 1.78	Sn 1.96	Sb 2.05	Te 2.1	I 2.66	Xe
6	Cs 0.79	Ba 0.89	Tl 1.8	Pb 1.8	Bi 1.9	Po 2.0	At	Rn

Figure 1F.12 and 2D.2

- Elements with **high ionization energies and high electron affinities**: highly electronegative
- Elements **with low ionization energies and low electron affinities**: low electronegativity.
- Careful: electropositive is used for a different concept and is NOT the opposite of electronegative.

2D.1 Correcting the covalent model: electronegativity

Two extremes

Small difference in electronegativity between atoms → small partial charge → resulting dipole moment is small

Covalent bond

Large difference in electronegativity between atoms → high partial charge → resulting dipole moment is large

Ionic bond



Continuum

No sharp dividing lines

2D.1 Correcting the covalent model: electronegativity

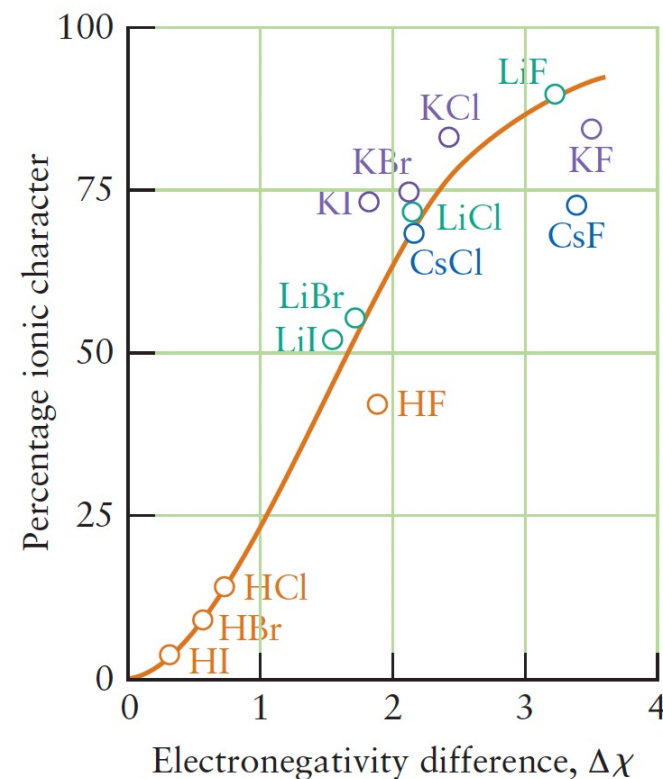
Rules of thumb for A-B bonds:

$(\chi_A - \chi_B) \geq 2$: Bond is *essentially ionic*

$0.5 \leq (\chi_A - \chi_B) \leq 1.5$: Bond is **polar covalent**

$(\chi_A - \chi_B) \leq 0.5$: Bond is *essentially covalent*

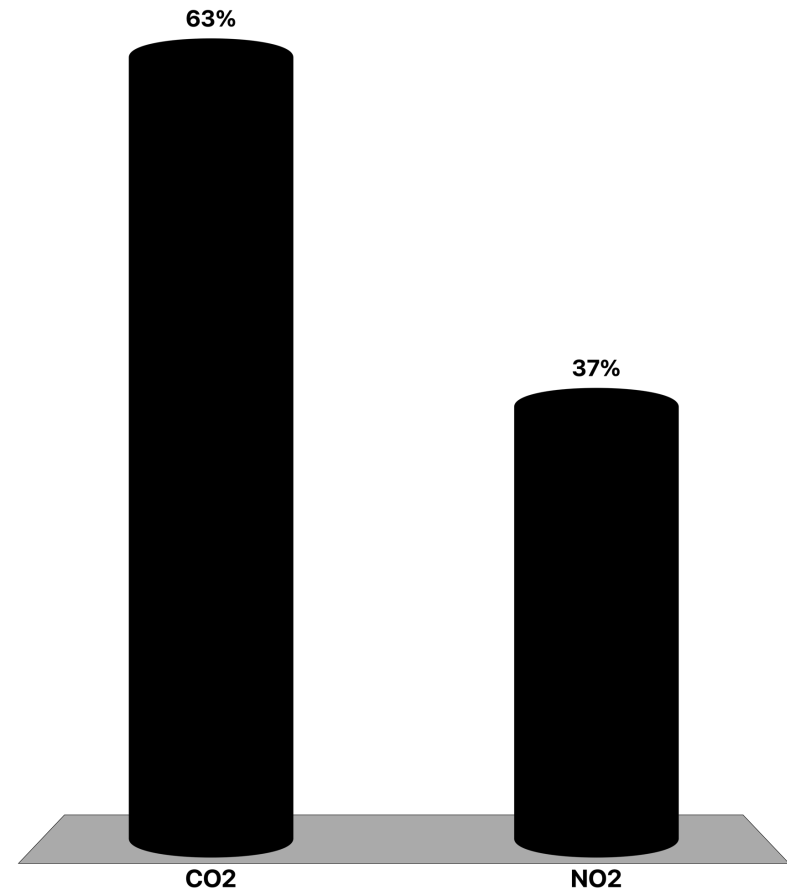
Figure 2D.3



In which of the following compounds do the bonds have greater ionic character:

A. CO₂ (correct)

B. NO₂



2D.1 Correcting the covalent model: electronegativity

Summary

Electronegativity is a measure of the pulling power of an atom on the electrons in a bond. A **polar covalent bond** is a bond between two atoms with partial electric charges arising from their difference in electronegativity. The presence of partial charges can give rise to an electric dipole moment.

Correcting the Ionic Model: Polarizability

Topic 2D.2

2D.2 Correcting the ionic model: polarizability

From the perspective of ionic bonds

- All have some covalent character.
- Monatomic anions (Cl^-) next to cations (Na^+): cation's positive charge pulls on anion's electrons
- Electron cloud becomes polarized
- Distortion of spherical electron cloud

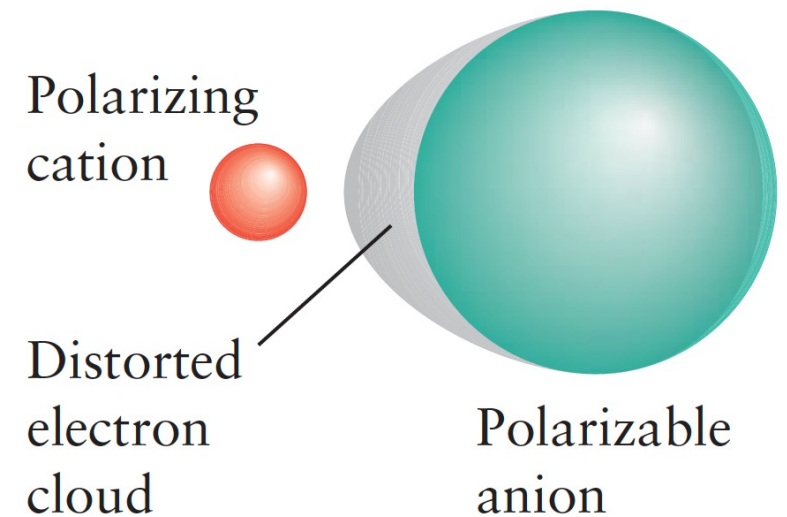


Figure 2D.4

2D.2 Correcting the ionic model: polarizability

Polarizable atoms and ions

- If atoms and ions have electron clouds that readily undergo large distortion, they are said to be **polarizable**.
- Examples: Large anions, e.g. iodide ion (I^-), Br^- , Cl^- , I, Br, Cl



2D.2 Correcting the ionic model: polarizability

Polarizing power

- Atoms and ions that cause large distortions are said to be **polarizing**.
- Polarizing power increases as size decreases and increases as charge of cation increases
- Examples: Small and highly charged cations, Li^+ , Be^{2+} , Mg^{2+} , and Al^{3+}



2D.2 Correcting the ionic model: polarizability

Trends

→ Cations get smaller and more highly charged from left to right → more polarizing

For example: Be^{2+} is more polarizing than Li^+

→ Cations get larger down a group → less polarizing

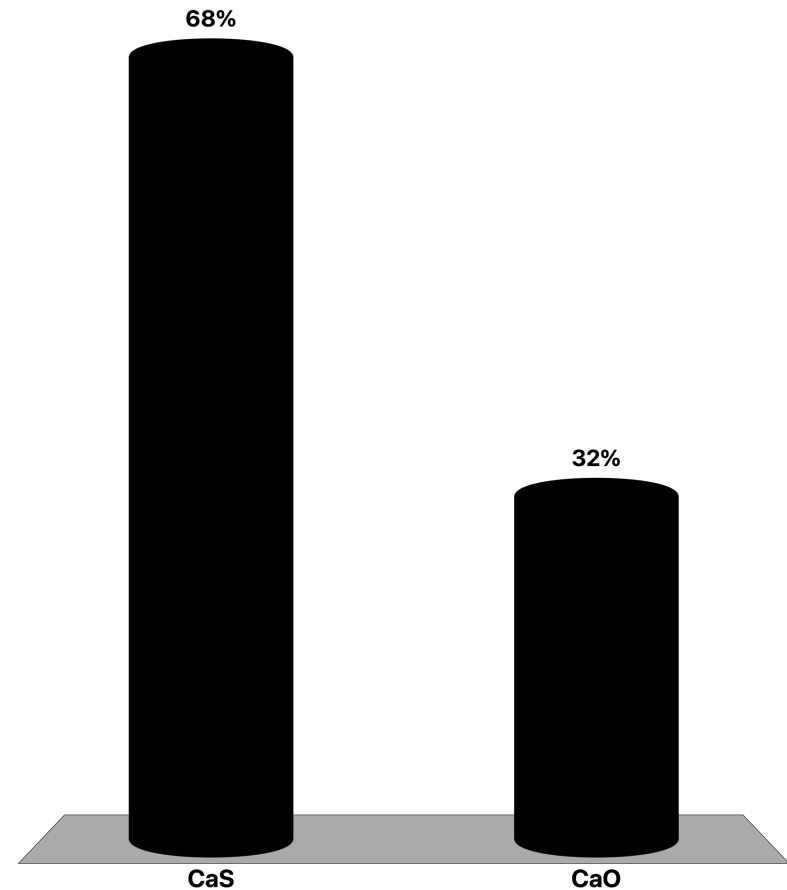
For example, Na^+ is less strongly polarizing than Li^+ , Mg^{2+} is less polarizing than Be^{2+}

Diagonal relationships: Polarizing power increases from Li^+ to Be^{2+} , decreases from Be^{2+} to Mg^{2+} . Li^+ and Mg^{2+} should be similar.

In which of the compounds CaS and CaO do the bonds have greater covalent character?

A. CaS (correct)

B. CaO



2D.1 Correcting the covalent model: electronegativity

Self-test 2D.2B

- In which of the compounds CaS and CaO do the bonds have greater covalent character?
- Solution: CaS
- Moving down a group, the bonds become more covalent as the polarizability (also size) of the anion increases ($\text{O}^{2-} < \text{S}^{2-}$). Same trend is true for $\text{Cl}^- < \text{Br}^- < \text{I}^-$

2D.2 Correcting the ionic model: polarizability

Summary

Compounds composed of highly polarizing cations and highly polarizable anions have significant covalent character in their bonding.